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Thermo-oxidative characterization and kinetics of tar sands

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ABSTRACT

In this research, non-isothermal kinetics and thermal analysis of *Gerçüş* tar sand sample is studied by DSC (differential scanning calorimeter) and TG/DTG (thermogravimetry). Experiments were performed using three different mesh size (20–35, 35–50 and >50) of sample. Differential scanning calorimeter (DSC) curves revealed three reaction regions in the temperature range of 20–600 °C. On the other hand, thermogravimetry (TG/DTG) curves of tar sand samples at different particle sizes demonstrated three stages of weight loss. Two different kinetic models (Coats & Redfern and Arrhenius) were used to determine the kinetic parameters of the samples and it was observed that the average activation energy values were between 17.5 and 26.6 kJ/mol, for reaction region-II and 126.2–160.1 kJ/mol for reaction region-III, respectively. In order to see the contribution of each region to the overall reactivity of the tar sand sample, weighted mean apparent activation energy of the samples are also determined.

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1. Introduction

Tar sands are naturally occurring bitumen-impregnated sands that yield mixtures of liquid hydrocarbon and that require further processing other than mechanical blending before becoming finished petroleum products. Tar sands are rocks (other than coal or oil shale) that contain highly viscous hydrocarbons that are unrecoverable by primary production methods. Thermo-analytical methods, such as TG/DTG (thermogravimetry), DSC (differential scanning calorimeter) and DTA (differential thermal analysis) have proved to play an important role in the characterization and combustion studies of fossil fuels, including tar sands [1–5].

Tonbul et al. [6] studied the thermal behavior of asphaltites using thermogravimetric analysis at atmospheric pressure. TG/DTG data of samples demonstrated two stages of mass loss. The first stage, called primary volatilization, occurred in the temperature range of 200–600 °C. On the other hand, secondary gasification stage occurred, in the temperature range of 600–800 °C. *Kok* et al. [7] studied the combustion characteristics and reaction kinetics of *Silopi* region asphaltites. Product gas analyses were used to determine the atomic H/C ratio, relative reaction rate, activation energy and Arrhenius constant for each asphaltite sample studied. In the low temperature region, an early production of oil was observed where the volatiles within the asphaltite were released. Remaining heavy hydrocarbons caused the formation of high temperature oxidation region. *Ballica* [8] studied the oxidation of *Şırnak* asphaltite samples under isothermal conditions using a fixed-bed reactor in various temperature modes. The effect of heating rate on reaching final isothermal temperatures was investigated. Kinetic parameters of the overall oxidation reaction for each heating rate were also determined. *Kok* [9] studied the non-isothermal combustion and kinetics of *Silopi* asphaltite samples by differential scanning calorimeter (DSC) and thermogravimetry (TG/DTG). In all the experiments, two reaction regions were observed. The first region was due to the evaporation of moisture in asphaltite sample. The second region was due to release of volatile matter and burning of carbon. *Elbeyli* [10] studied the pyrolysis properties and kinetic analysis of asphaltite samples by means of thermogravimetry (TG/DTG). Thermogravimetric curves showed that the decomposition proceeds through two steps. Coats-Redfern method was used to analyze the TG/DTG data for the determination of kinetic parameters for different heating rates. *Hiçyılmaz and Altun* [11] studied the *Şırnak* asphaltite samples by gravity and flotation methods. Combustion of raw and improved asphaltites was performed by non-isothermal thermogravimetric experiments. Activation energies were correlated with ash contents, calorific values, bum-out temperatures and sulfur contents of the samples. *Al-Ottom* et al. [12] studied the different parameters affecting the behavior of flotation of Jordanian tar sand utilizing a fluidized bed floatator. The effects of the addition of a flotation agent, NaOH, temperature and flotation time on the beneficiation of bitumen in the froth were investigated. It was found that the beneficiation factor in the froth increased with the increase of temperature and flotation time. *Penner* et al. [13] reviewed and

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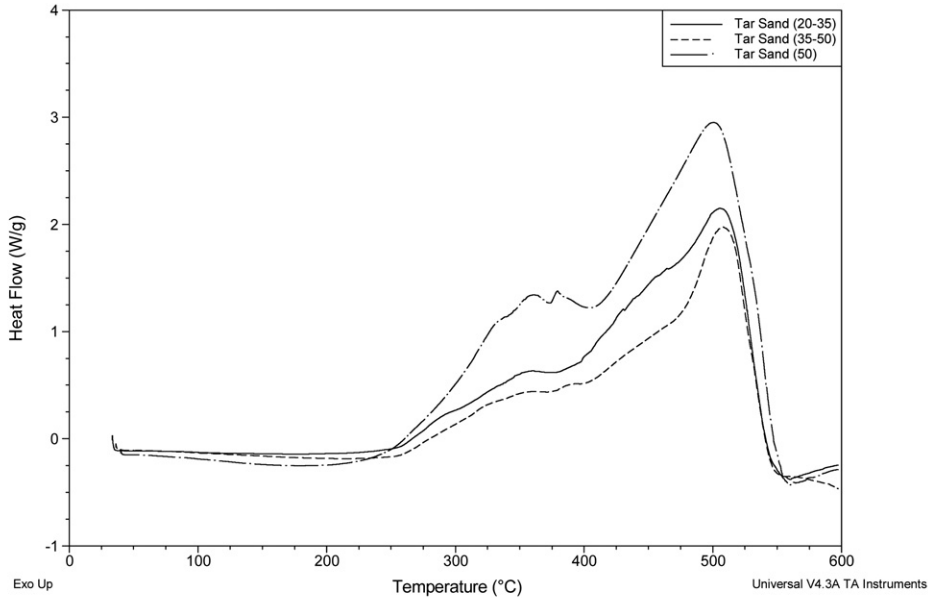

Fig. 1. DSC curves of tar sand sample of different mesh size.

evaluated the U.S. programs on oil recovery from heavy oil sources and tar sands. These studies were performed in order to provide an independent assessment of research areas that affect the prospects for oil recovery from these sources. *Alkhamis and Kablan* [14] designed a process to produce carbonaceous matter from combinations of tar sand, oil shale and olive cake. The minimum temperature to achieve complete carbonization was found to be 500 °C for a minimum heating time of 90 min. Overall results indicate that the process is successful in producing carbonaceous matter. *Al-Ottom* et al. [15] studied the utilization of a modified fluidized froth flotation process for beneficiation and bitumen recovery from oil sands. Results of this research show that the recovery of bitumen from Jordanian oil sand reaches its maximum of 86% during the addition of 0.35 wt % of a special cut of light cycle oil as a collector. The results show that the amount of hydrocarbon content in oil sand has a minimal impact on floatability of oil sand.

2. Materials and methods

The *Gerçüş* tar sand sample used throughout the research was from south-eastern part of Turkey (Calorific value: *1266 kcal/kg*; Ash content: *45.9%*; Volatile matter: *52.4%*; Fixed carbon: *1.69%*; Moisture content: *0.17%*). Organic matter type of *Gerçüş* tar sand is petroleum origin; whereas inorganic materials are sandstone (quartz) and clay-stone. Solid bitumen bearing sandstone from the *Gerçüş* formation is composed of quartz, feldspar albite, dolomite and clay minerals. Metamorphic aspaltic substances have been found in numerous places in fissures and sometimes impregnated into permeable rocks. Organic and inorganic matter content is 35% and 62% respectively. TOC (total organic carbon) value of solid bitumen bearing sandstone is 9.3% wt, T_{max} value is 428 °C and hydrogen index is 584 mgHC g^{-1}. Maximum reflectance (R_{max}) values of *Gerçüş* tar sand sample varied between 0.43 and 0.46% [16].

In this research, experiments were performed with *TA* 2000 thermal analysis system with differential scanning calorimeter (DSC) and thermogravimetry (TG/DTG) modules. The tar sand sample used in this research is prepared according to the ASTM Standards (D 2013-72) at three different mesh sizes (20–35, 35–50 and >50). The experiments are carried out with the powdered sample ($\sim$10 mg) whereas the air flow rate (50 ml min^{-1}) was kept constant during the experiments. All the experiments were conducted in the temperature range of 20–600 °C (DSC) and 20–900 °C (TG/DTG) at 10 °C min^{-1} heating rate. Reproducibility of the experiments was acceptable and the experimental data presented corresponds to the different operating conditions are the mean values of the runs carried out twice within the experimental error of less than ±0.5%.

3. Results and discussion

Theoretically combustion of oil can be initiated whenever oxygen comes in contact with fuel. However, the temperature, composition of the fuel and the oxygen supply dictate the nature of this reaction.

In combustion of *Gerçüş* tar sand, differential scanning calorimeter (DSC) curves revealed two reaction regions in the temperature range of 20–600 °C (Figure 1). The first stage is a relatively light organic substance volatilizing and desorbing from 200 to 425 °C; and the second stage is between 425 and 560 °C, where a relatively heavy organic substances cracks.

In differential scanning calorimeter (DSC) experiments, heat flow rates of the samples at different particle sizes are also determined. It observed that the heat flow rates are varied between 48 and 89 J/g in the second region and 812–1279 J/g in the third region, respectively (Table 1).

Table 1
Reaction regions (°C) and heat flow rates (J/g) of the samples of different mesh size (DSC).

Mesh size	Stage-1	Stage-2	Stage-3
Reaction regions (°C)			
>50 mesh	<200	200–400	400–550
35–50 mesh	<200	200–395	395–545
20–35 mesh	<200	200–380	380–540
Heat flow rates (J/g)			
>50 mesh	n.a.	89	1279
35–50 mesh	n.a.	48	812
20–35 mesh	n.a.	87	1052

n.a. not available.

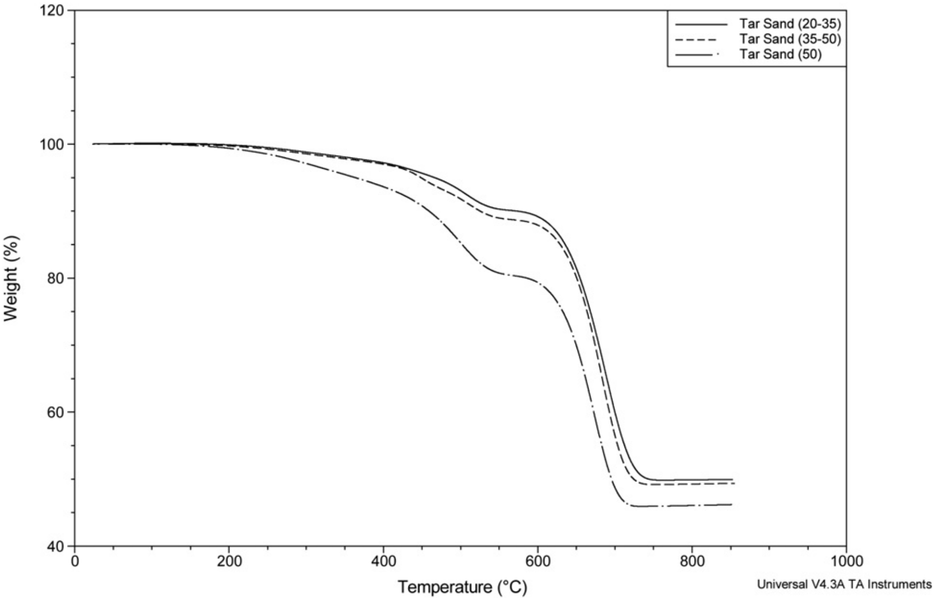

Fig. 2. TG curves of tar sand sample of different mesh size.

TG/DTG curves of tar sand samples at different particle sizes demonstrated three stages of weight loss (Figs. 2 and 3) (Table 2). The first stage is below 200 °C, where water volatilizes and low-molecular mass species takes place in this stage. In the second stage, owing to the temperature rise, relatively light organic substance volatilizing and desorbing from 200 to ~400 °C. The third stage, in the temperature range of ~400–575 °C, is attributed to the cracking of heavy organic substances and combustion of remaining hydrocarbons and carbon residue. An isolated reaction following the third stage in the temperature range of ~575–750 °C, may be due to a decomposition of some inorganic matter (Table 3).

3.1. Kinetic analysis

The non-isothermal kinetic study of weight loss during a combustion process is extremely complex, because of the presence of numerous components and their parallel and consecutive reactions.

In kinetic analysis of the tar sand samples, *Coats & Redfern* [17] model is used to analyze the TG/DTG curves. For simplicity, a reaction order (n) is assumed to be unity ($n = 1$) and used to integrate the equation. This simplification will not diminish the generality of the *Coats & Redfern* approximation, because this technique applies only to the right-hand side of the final equation (Eq. 7). In practice, the determination of kinetic parameters for a reaction requires a three-parameter search: reaction order, activation energy, and frequency factor. In this model, the rate of disappearance of sample may be expressed by:

$$d\alpha/dt = k(1-\alpha)^n \qquad (1)$$

where: $\alpha = (W_{initial} - W_T)/(W_{initial} - W_{final})$

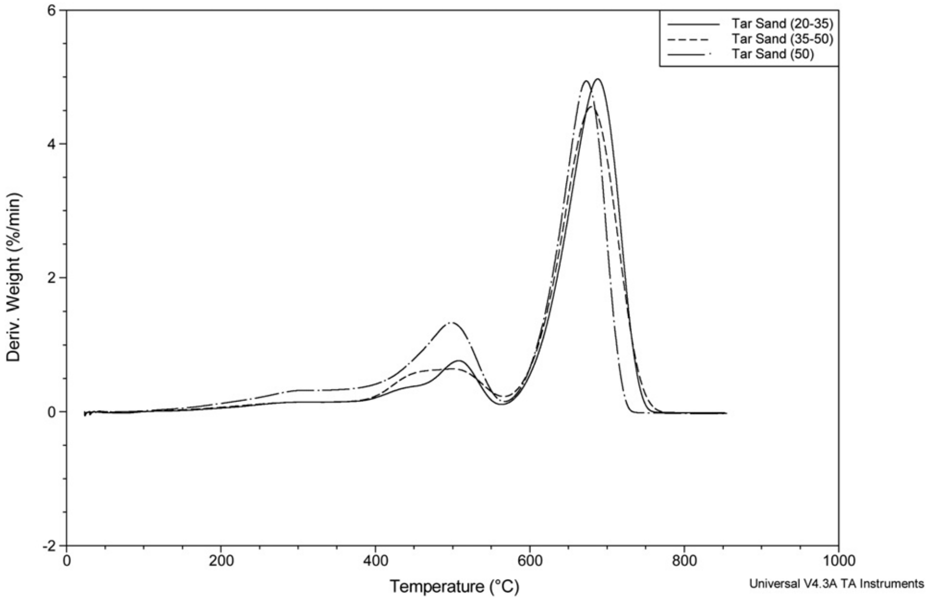

Fig. 3. DTG curves of tar sand sample of different mesh size.

Table 2
Reaction regions (°C) of the samples of different mesh size (TG/DTG).

Mesh size	Stage-1	Stage-2	Stage-3
>50 mesh	<200	200–400	400–570 570–730
35–50 mesh	<200	200–395	395–565 565–740
20–35 mesh	<200	200–385	385–575 575–790

Table 3
Peak and burn-out temperatures (°C) of the samples of different mesh size (TG/DTG).

Mesh size	Peak temp. (Stage-1)	Peak temp. (Stage-2)	Peak temp. (Stage-3)	Burn-out temp.
>50 mesh	n.a.	315	495 675	730
35–50 mesh	n.a.	300	485 685	740
20–35 mesh	n.a.	290	505 700	750

n.a. not available.

Table 4
Activation energies (kJ/mol) of the samples of different mesh size (10 °C/min. Heating rate, TG/DTG).

Mesh size	Activation energy (Stage-2)	Activation energy (Stage-3)
Coats and Redfern method		
>50 mesh	24.8	136.1
35–50 mesh	24.3	160.1
20–35 mesh	26.5	150.3
Arrhenius method		
>50 mesh	17.5	126.2
35–50 mesh	21.4	158.1
20–35 mesh	25.8	152.5

$$k = A\exp(-E/RT) \tag{2}$$

For a linear heating rate, say, β deg/min

$$\beta = dT/dt \tag{3}$$

Combining Equation (1)–(3), rearranging and integrating,

$$d\alpha/(1-\alpha)^{n} = A/\beta e^{-E/RT}dT \tag{4}$$

The right-hand side of the Equation (4) has no exact integral, but by making the substitution and integration, the equation takes the following form.

$$1-(1-a)^{1-n}/(1-n) = ART^{2}/\beta E(1-2RT/E)e^{-E/RT} \tag{5}$$

Taking logarithms of each side,

$$\log\left[\left(1-(1-\alpha)^{1-n}/\left(T^{2}(1-n)\right)\right)\right] = \log[(AR/\beta E)\ (1-2RT/E)] - \ [E/(2.303RT)] \tag{6}$$

for all values of n except $n = 1$. When reaction order equals to one, the above equation takes the following form;

$$\log\left[-\log(1-\alpha)/T^{2}\right] = \log[(AR/\beta E)\ (1-2RT/E)] - [E/(2.303RT)] \tag{7}$$

Thus a plot of either, log $[(1-(1-\alpha)^{1-n})/(T^{2}(1-n))]$ vs. 1/T or, log $[-\log(1-\alpha)/T^{2}]$ vs. 1/T, should result in a straight line in which the slope is equal to $-E/2.303R$ for the correct value of reaction order.

From the numerical results, it is evident that the *Coats & Redfern* technique will produce a straight line from conversion vs. temperature data for all the data sets. A statistical analysis of the regression for the model for these data sets has given values of R^2 of 0.99. F-tests also confirm the predictions of a linear correlation for this technique.

Activation energy values of the tar sand sample of different mesh size for the reaction regions were determined using the above mentioned procedure (Table 4). It was observed that the average activation energy values were in the range of 24.8–26.6 kJ/mol, for reaction region-II and 136.1–160.1 kJ/mol for reaction region-III, respectively. It can be concluded that, no changes were observed in the activation energies of the tar sand sample of different mesh size.

In *Arrhenius* model [18,19], it is assumed that the rate of weight loss of the total sample is dependent only on the rate constant, the weight of the sample remaining and the temperature with reaction order of unity. The final form of the equation is as follows:

$$\log[(d\,W/d\,t)/W] = \log A_r - E/2.303\ RT \tag{8}$$

Where; dW/dt is the rate of weight change, E is the activation energy, T is the temperature and A_r is Arrhenius constant. When log [(dW/dt)/W] is plotted against 1/T, a straight line is obtained which

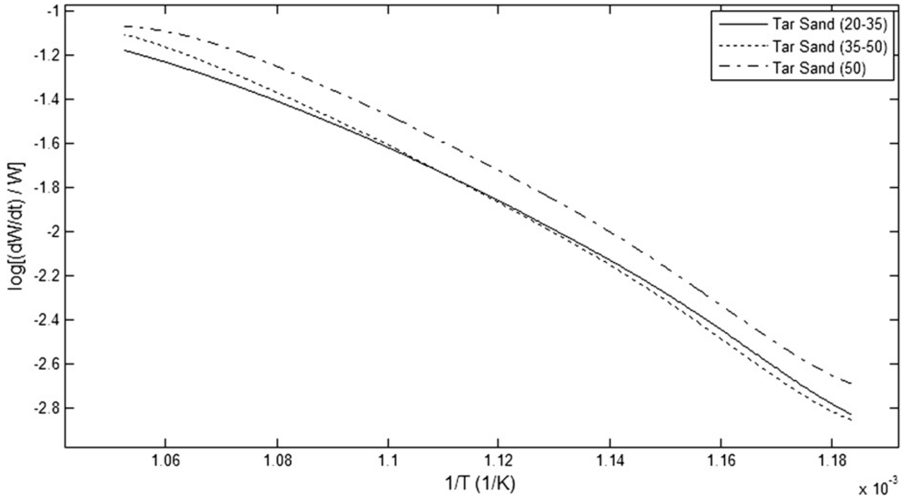

Fig. 4. Arrhenius plot (Stage-3) of tar sand sample of different mesh size.

Table 5
Mean activation energy (kJ/mol) of the samples of different mesh size (10 °C/min. Heating rate, TG/DTG).

Mesh size	Mean activation energy
Mean activation energy (Coats and Redfern method)	
>50 mesh	50.4
35–50 mesh	65.0
20–35 mesh	62.2
Mean activation energy (Arrhenius method)	
>50 mesh	45.8
35–50 mesh	63.7
20–35 mesh	63.1

will have a slope equal to E/2.303R where activation energy can be obtained (Figure 4).

It was observed that for different mesh sizes of tar sand sample, the average activation energy values were in the range of 17.5–25.8 kJ/mol, for reaction region-II and 126.2–152.5 kJ/mol for reaction region-III, respectively (Table 4). These values are in good order with the values obtained from *Coats & Redfern* method.

Although these values define the apparent activation energies associate with the various stages of the combustion process, they say nothing about the overall reactivity of the fuel, since they do not incorporate any term relating to the amount of sample reacted during each stage. The individual values of activation energy values can be attributed to different reaction mechanisms coming into play as the temperature is increased, but they do not give any indication of the contribution of each region to the overall reactivity of the fuel. To meet this requirement, the concept of weighted mean apparent activation energy has been adopted, and in this particular case, this is calculated as follows [20]:

$$E_m = F_1 \times E_1 + F_2 \times E_2 + \ldots + F_n \times E_n \qquad (9)$$

where; F_1 to F_n are the weight fractions of the combustible content of the samples burned during each region of Arrhenius linearity, and E_1 to E_n are the individual values of apparent activation energy obtaining over each corresponding period of Arrhenius linearity (Table 5).

4. Conclusions

In this research, non-isothermal thermal analysis and kinetics of *Gerçüş* tar sand sample is determined using thermal analysis techniques. DSC and TG/DTG curves revealed three reaction stages known as water volatilization, volatilization of organic substances and cracking of heavy organics. *Coats & Redfern* and *Arrhenius* kinetic models were applied and it was observed that the average activation energy values were between 17.5 and 26.6 kJ/mol, for reaction region-II and 126.2–160.1 kJ/mol for reaction region-III, respectively. Weighted mean apparent activation energy of the samples is also determined in order to see the contribution of each region to the overall reactivity of the tar sand samples.

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